

Modeling the impacts of decadal changes in riverine nutrient fluxes on coastal eutrophication near the Mississippi River Delta

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Abstract

A mathematical model was used to link decadal changes in the Mississippi River nutrient flux to coastal eutrophication near the Mississippi River Delta. Model simulations suggest that bottom water hypoxia intensified about 30 years ago, as a probable consequence of increased net productivity and increased sedimentation of the organic material produced in situ in the upper water column. Model simulations also suggest that long-term increase in riverine nutrient fluxes has been responsible for this historical decrease in bottom layer oxygen concentrations. Importantly, model simulations are in good agreement with the available historical data from the northern Gulf of Mexico, and are additionally supported by the retrospective analyses of sedimentary records. Conclusively, this modeling study supports the hypothesis that riverine nutrient fluxes, via their influence on net productivity of the upper water column, play a major role in controlling the development of bottom water hypoxia and accumulation of organic carbon in coastal sediments. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Eutrophication, the manifestation of nutrient-enhanced aquatic primary productivity, often indicated by the presence of noxious phytoplankton blooms and bottom water hypoxia, has been reported from a variety of estuarine and coastal

environments (Officer et al., 1984; Rosenberg, 1985; Westernhagen et al., 1986; Benović et al., 1987; Justić et al., 1987; Andersson and Rydberg, 1988; Smayda, 1990; Cooper and Brush, 1991; Hickel et al., 1993; Turner and Rabalais, 1994; Justić et al., 1995a; Rabalais et al., 1996, 1999). The extent and severity of this phenomenon has increased substantially over the last several decades, most likely in response to increased anthropogenic inputs of nitrogen (N) and phosphorus (P), and more balanced stoichiometric

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nutrient ratios in freshwaters (Marchetti et al., 1989; Turner and Rabalais, 1991; Dortch and Whitledge, 1992; Justić et al., 1995a,b; Howarth et al., 1996; Turner et al., 1998).

Coastal waters of the northern Gulf of Mexico (Fig. 1) are classic examples of these phenomena. The concentrations of total P and dissolved inorganic N in the Mississippi River have increased two-fold and three-fold, respectively, during the last 40–50 years (Turner and Rabalais, 1991). The impacts of changing riverine nutrient fluxes and nutrient ratios have been far reaching, affecting not only primary productivity, but also the productivity of higher trophic levels (Turner and Rabalais, 1994; Turner et al., 1998; Rabalais et al., 1999). The northern Gulf of Mexico is presently the site of the largest (up to 20 000 km²) and most severe coastal hypoxic zone in the western Atlantic Ocean (Rabalais et al., 1996, 1999). Hypoxia typically occurs from April through September in waters below the pycnocline, and extends to water depths of 60 m (Rabalais et al., 1991, 1999). Hypoxia is a synergistic product of high surface primary productivity, which is also manifested in a high carbon flux to the sediments, and high stability of the water column (Rabalais et al., 1991; Wiseman et al., 1999).

The pervasive influence of the Mississippi River on coastal productivity is most clearly evident during the years when the freshwater discharge is higher than normal. During the flood of 1993, for

example, nutrient concentrations, phytoplankton biomass, and net productivity were greatly increased (Dortch, 1994; Justić et al., 1997; Rabalais et al., 1998). As a result, the average areal extent of the summertime hypoxic zone showed a two-fold increase with respect to the average hydrologic year (Fig. 1). The opposite occurred during the drought of 1988 when bottom oxygen concentrations were significantly higher than normal, and formation of a continuous hypoxic zone did not develop (Fig. 1, Rabalais et al., 1999).

There is an extensive body of literature on different classes of water quality models that include dissolved oxygen as a state variable (e.g. Bowie et al., 1985; Jorgensen, 1986). There has also been a widespread use of dynamic oxygen models in case studies of lakes (e.g. Jorgensen, 1976; Jorgensen et al., 1978; Asaeda and Bon, 1997) and coastal waters (e.g. Stigebrandt and Wulff, 1987; Aksnes and Lie, 1990; Justić, 1991; Legović and Justić, 1997; Chapelle et al., 2000). In a related study, Bierman et al. (1994) developed a deterministic mass balance model for phytoplankton, nutrients and dissolved oxygen, and applied this model to the inner shelf region of the northern Gulf of Mexico.

Here we use a coupled physical–biological model to simulate decadal changes in the oxygen and carbon budgets in coastal waters adjacent to the Mississippi River Delta. The model formulation is in part based on our published two-box

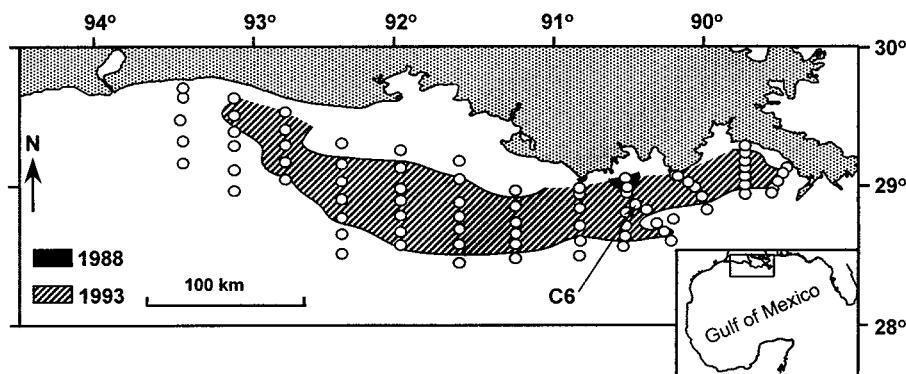


Fig. 1. The map of the study area showing the station grid and location of station C6. Shaded areas represent the distribution of hypoxic ($< 2 \text{ mg O}_2 \text{ l}^{-1}$) bottom waters during August 1988 and July 1993. Note that during August 1988 hypoxia was observed only at the inshore end of the transect C.

model (Justić et al., 1996) used to assess the potential impacts of global climate change on vertical oxygen fluxes in the northern Gulf of Mexico (Justić et al., 1997). The revised model used in this study includes a number of additional mathematical formulations that are critical for describing the eutrophication process. Our objectives are, (1) to test the robustness of a simple eutrophication model in reproducing and predicting the ecosystem processes on annual and decadal time scales; (2) to use this model and retrospective analyses of sedimentary records to quantitatively describe temporal changes in benthic-pelagic coupling, and; (3) to test the hypothesis that riverine nutrient flux, via its influence on net productivity, is a controlling factor in the development of hypoxia and accumulation of organic carbon in coastal sediments.

2. Area of study

The study area encompasses shallow (~ 20 m) waters of the northern Gulf of Mexico continental shelf (Fig. 1). Station C6, located in the inner section of the hypoxic zone was used as a reference site. This site was chosen because it has the longest and most consistent oceanographic data records (1985, present) for this region. The northern Gulf of Mexico (Fig. 1) is strongly influenced by the Mississippi river, one of the largest world rivers (Milliman and Meade, 1983), and the Atchafalaya river. Their combined discharges account for 98% of the total freshwater input into the northern Gulf of Mexico (Dinnel et al., 1986). The average annual discharge of the two rivers between 1950 and 1996 was around $20\,000\text{ m}^3\text{ s}^{-1}$ (Goolsby et al., 1999).

The Mississippi River Delta has prograded to the shelf break and much of the water from this delta discharges into deep waters (Wiseman et al., 1999). As a result, the buoyant freshwater plume lifts off the bottom and expands rapidly as soon as it leaves the river mouth (Wiseman et al., 1995). The nutrient-rich plumes of the Mississippi and the Atchafalaya rivers tend to initially flow in a clockwise direction until they encounter the Louisiana coast. At that point they contribute to

the Louisiana coastal current that flows predominantly westward along the Louisiana coast, and then southward along the Texas coast. Riverine nutrients are confined to the upper 10 m by a strong seasonal pycnocline ($\Delta\sigma_t = 4\text{--}10\text{ kg m}^{-3}$), which normally persists from March through September (Rabalais et al., 1991, 1999). Mean winds in this region of the Gulf of Mexico are generally from the southeast during most of the year. During the summer months, however, southerly winds along the Texas coast tend to push the water back onto the Louisiana shelf. This wind reversal is important because it may reverse the flow of the Louisiana coastal current for a month to 6 weeks at a time (Wiseman et al., 1997).

3. Model formulation

3.1. Applicability of a two-box modeling scheme

We adopted our previously published two-box modeling scheme (Justić et al., 1996), which assumes uniform properties for the layers above and below the average depth of the pycnocline. Three distinct oceanographic features of this region facilitated the application of a two-box modeling scheme: (1) between the beginning of April and the end of September, a strong pycnocline ($\Delta\sigma_t = 4\text{--}10\text{ kg m}^{-3}$) is typically found at the average depth of 10 m (Rabalais et al., 1991). Since the water depth is only about 20 m, the pycnocline virtually divides the upper and the lower water column into two distinct water bodies of approximately equal volumes. (2) The horizontal oxygen transport in the inner section of the hypoxic zone appears to be of lesser importance than the vertical oxygen transport. This is suggested by a high coherence between changes in vertical temperature gradients and changes in bottom oxygen concentration. In contrast, a strong tidal signal, which would indicate horizontal transport, is not present in the periodograms of oxygen data series from station C6 (Rabalais et al., 1994). (3) The maximum lateral displacement of water parcels that can be expected due to diurnal and semidiurnal currents in the study area is only about 3 km (Rabalais et al., 1994), which is not likely to affect the inner section of a 60 km wide hypoxic zone.

Table 1
Description of state variables and model parameters

State variable or parameter	Units
C_s , the pool of sedimentary organic carbon	g C m^{-2}
D_O , diffusive oxygen flux through the pycnocline	$\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$
ε , turbulent kinetic energy dissipation rate	$\text{m}^2 \text{ s}^{-3}$
E_c , loss of sedimentary carbon due to the resuspension and export	$\text{g C m}^{-2} \text{ day}^{-1}$
F_{Ot} , total air–sea oxygen flux	$\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$
g , acceleration due to gravity ($= 9.81 \text{ m s}^{-2}$)	m s^{-2}
k , decay constant	day^{-1}
K_z , vertical eddy diffusivity	$\text{m}^2 \text{ s}^{-1}$
N , buoyancy frequency	s^{-1}
NP, net productivity of the upper water column	$\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$
O_2 , oxygen concentration	$\text{g O}_2 \text{ m}^{-3}$
O_2^s , oxygen saturation value	$\text{g O}_2 \text{ m}^{-3}$
O_s , average oxygen concentration in the upper water column	$\text{g O}_2 \text{ m}^{-3}$, ($\text{mg O}_2 \text{ l}^{-1}$)
O_{ts} , total oxygen content of the upper water column	$\text{g O}_2 \text{ m}^{-2}$
O_b , average oxygen concentration in the lower water column	$\text{g O}_2 \text{ m}^{-3}$, ($\text{mg O}_2 \text{ l}^{-1}$)
O_{tb} , total oxygen content of the lower water column	$\text{g O}_2 \text{ m}^{-2}$
Q , river runoff	$\text{m}^3 \text{ s}^{-1}$
R , respiration rate in the lower water column	$\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$
ρ , density	kg m^{-3}
ρ_w , average density of the water column	kg m^{-3}
S_f , vertical carbon flux	$\text{g C m}^{-2} \text{ day}^{-1}$
Sc , Schmidt number	
t , time	days
T_b , average temperature in the lower water column	$^{\circ}\text{C}$
T_s , average surface temperature	$^{\circ}\text{C}$
V , transfer velocity	m day^{-1}
W , wind speed	m s^{-1}
z , depth	m

Respective parameter values that are used in simulations are explained in the text.

3.2. The governing equations

The model includes mathematical descriptions of relevant physical and biological processes that affect oxygen cycling in shallow, river-dominated, coastal waters (Justić et al., 1996, 1997). The

oxygen concentration in the upper water column changes as a result of biological oxygen production and consumption, oxygen transport in the horizontal and vertical direction, and atmospheric exchanges. By neglecting horizontal oxygen transport due to advection and diffusion, the oxygen balance in the upper water column (O_{ts} , $\text{g O}_2 \text{ m}^{-2}$, 0–10 m) may be described by the expression:

$$\frac{\partial O_{ts}}{\partial t} = -F_{Ot} - D_O + \text{NP} \quad (1)$$

where t is time (day), F_{Ot} is the total air–sea oxygen flux ($\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$), D_O is the diffusive oxygen flux through the pycnocline ($\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$), and NP is the net primary productivity expressed in terms of oxygen equivalents ($\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$). Due to the high turbidity of the continental shelf waters near the Mississippi river, primary productivity below the depth of 10 m is low (Lohrenz et al., 1990), and may be considered an insignificant term when compared with vertical oxygen transport. Thus, the balance equation for oxygen in the lower water column (O_{tb} , $\text{g O}_2 \text{ m}^{-2}$, 10–20 m) includes only two terms, oxygen uptake due the benthic and water column respiration (R), and oxygen resupply from the upper water column via turbulent diffusion (D_O):

$$\frac{\partial O_{tb}}{\partial t} = -R + D_O \quad (2)$$

A description of the individual model terms from Eqs. (1) and (2) is discussed below. A concise description of state variables and model parameters is in Table 1.

3.2.1. Air–sea oxygen flux (F_{Ot})

Oxygen transport through the sea surface is dependent on the difference in the partial pressure of the gas in the surface layer and in the atmosphere. The transfer velocity across the air–sea boundary is thought to be a function of the temperature and the wind speed. In our calculations we used the formulation proposed by Stigebrandt (1991), which takes into account the effect of gas transfer due to bubbles:

$$F_{Ot} = V(O_s - 1.025O_2^s) \quad (3)$$

Here F_{Ot} is the total air–sea oxygen flux ($\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$), V is transfer velocity (m day^{-1}), O_s is the average surface oxygen concentration ($\text{g O}_2 \text{ m}^{-3}$, 0–10 m), and O'_2 is the oxygen saturation value ($\text{g O}_2 \text{ m}^{-3}$). Negative F_{Ot} values obtained from Eq. (3) indicate that the oxygen flux is directed towards the water column. The O_s value was computed by dividing the O_{ts} value (Eq. (1)) with the thickness of the upper water column (10 m). The oxygen saturation value was computed from the observed temperature data and estimated salinity values using the equation of Weiss (1970). Surface salinity values for station C6 were calculated from the Mississippi River runoff data, using a time-delayed linear model ($\tau = 2$ months, $r^2 = 0.8$, $P < 0.001$) developed by Justić et al. (1996). The transfer velocity was computed from a formula given by Liss and Merlivat (1986):

$$V = 5.9Sc^{-0.5}(aW + b) \quad (4)$$

where Sc is Schmidt number, and W is wind speed (m s^{-1}). The values of constants a and b depend on the wind speed. In the interval where $3.6 < W < 13 \text{ m s}^{-1}$ these constants are equal to 2.85 and -9.65 , respectively (Liss and Merlivat, 1986). At oxygen saturation levels above 125%, a modification of Eq. (4) was used that takes into account the oxygen surplus:

$$V = 5.9Sc^{-0.5}(aW + b)\left(\frac{O_s}{O'_2}\right)^2 \quad (5)$$

where O_s is the ambient surface oxygen concentration ($\text{g O}_2 \text{ m}^{-3}$, 0–1 m), and O'_2 is the oxygen saturation value ($\text{g O}_2 \text{ m}^{-3}$). Schmidt numbers for oxygen were computed from surface temperature data (T_s), using a simple analytical expression derived by Stigebrandt (1991):

$$Sc = 1450 - 71T_s + 1.1T_s^2 \quad (6)$$

3.2.2. Oxygen flux through the pycnocline (D_O)

The vertical diffusive flux of oxygen (D_O) was estimated from the equation:

$$D_O = -K_z \left(\frac{\partial O_2}{\partial z} \right) \quad (7)$$

where K_z is the vertical eddy diffusivity ($\text{m}^2 \text{ s}^{-1}$), O_2 is ambient oxygen concentration ($\text{g O}_2 \text{ m}^{-3}$),

and z is depth (m). The model assumes that the only properties of the stratified water column controlling K_z are the turbulent kinetic energy dissipation rate (ϵ), and the buoyancy frequency ($=$ Brunt–Väisälä frequency) (N):

$$K_z = a\epsilon N^{-2} \quad (8)$$

Various values for parameter a have been suggested (e.g. Denman and Gargett, 1983). Due to the high stability of the water column in the northern Gulf of Mexico (Rabalais et al., 1999), we adopted the value of 0.8 (Weinstock, 1978). This value is thought to be valid for strong and intermediate stratification, where the Cox number is less than 2500 (Caldwell et al., 1980). We assumed that the turbulent energy dissipation rate (ϵ) at the depth of 10 m is in the range of $10^{-7} \text{ m}^2 \text{ s}^{-3}$, which is likely to be an upper estimate. Corresponding values were obtained from microstructure measurements in the upper ocean during high winds (Dillon and Caldwell, 1980). Buoyancy frequency N (s^{-1}) was calculated from the expression:

$$N^2 = \left(\frac{g}{\rho_w} \right) \left(\frac{\partial \rho}{\partial z} \right) \quad (9)$$

where g is the acceleration due to gravity (9.81 m s^{-2}), ρ_w is the average density of the water column (kg m^{-3}), and $\partial \rho / \partial z$ is the vertical density gradient (kg m^{-4}) between the upper (0–10 m) and the lower (10–20 m) water column. Vertical density gradients were computed from a multiple regression of $\partial \rho$ on salinity and temperature ($r^2 = 0.85$, $P < 0.001$), as explained in Justić et al. (1996).

3.2.3. Net productivity of the upper water column (NP)

The net productivity of the surface water column (NP, $\text{g C m}^{-2} \text{ day}^{-1}$) was computed from the time-delayed regression model developed by Justić et al. (1996):

$$\text{NP}_t = -0.34 + 3.93 \times 10^{-7}(\text{N-NO}_3)_{t-1} \quad (10)$$

where N-NO_3 is the nitrate flux of the Mississippi River (10^6 kg day^{-1}), and subscripts t and $t-1$ denote the current and the preceding month, respectively.

Nitrogen is often considered to be the limiting nutrient for the growth of estuarine and coastal phytoplankton (e.g. D'Elia et al., 1986). An analysis of the 1985–1991 data subset from the northern Gulf of Mexico suggested that the frequency of stoichiometric nitrogen limitation was on the order of 30% (Justić et al., 1995a,b). Stoichiometric nitrogen limitation was likely even more pronounced 40–50 years ago. This is because the historical increase in dissolved inorganic N in the lower Mississippi River was far more pronounced relative to the increase in total P. As stated previously, the concentrations of dissolved inorganic N and total P have increased three-fold and two-fold, respectively, during the last 40–50 years (Turner and Rabalais, 1991).

The Eq. (10) was developed based on the Mississippi River nitrate flux data for the period 1985–1992 and net productivity estimates at station C6. The cross correlation coefficient (ccc) indicated that the two time series are highly coherent (ccc = 0.73; $P < 0.01$), and that a time-delay of 1 month is justified (Justić et al., 1997). Conversion of carbon to oxygen equivalents, so that Eq. (1) is dimensionally correct, was carried out using a ratio of 3.47 by weight (mol. C:mol. O_2 = 106:138, Redfield et al., 1963).

3.2.4. Oxygen uptake in the lower water column (R)

The rate of respiration (R) in the lower water column is proportional to the amount of detritus present, and may be described by the first order decay relation:

$$R = -kC_s \quad (11)$$

where k is the decay constant, or respiration constant (per day), and C_s is the pool of sedimentary organic carbon that is available for decomposition ($g\ C\ m^{-2}$). Vertical flux of organic detritus to the bottom waters is described as a function of surface net productivity at some earlier time. For the northern Gulf of Mexico, Justić et al. (1993) showed that there is a significant coherence ($r = 0.85$, $P < 0.01$) between the net productivity of the upper water column (0–10 m) and the oxygen deficit in the lower water column (10–20 m), implying a time-lag of 1 month. Thus, the respira-

tion rate (R) in the lower water column at any given time t may be expressed in terms of the net productivity rate $NP(t)$ at some earlier time t_0 (Officer et al., 1984, 1985), so that:

$$R(t) = k(t) \int_{-\infty}^t \alpha NP(t_0) \exp\left[-\int_{-t_0}^t k(t_1) dt_1\right] dt_0 \quad (12)$$

where the proportionality constant α describes the fraction of NP that reaches the lower water column. Carbon uptake during respiration was converted to oxygen equivalents using a ratio of 3.47 by weight (mol. C:mol. O_2 = 106:138, $RQ = 0.77$, Redfield et al., 1963). Rabalais et al. (1991) suggested that around 50% of surface primary production may be reaching the bottom (~ 20 m on average) in the northern Gulf of Mexico. Based on the data for the period 1985–1992, Justić et al. (1997) estimated that the average respiration rate (R) of the lower water column (10–20 m) at station C6 accounted for 47% of the NP in the upper water column (0–10 m). Accordingly, a value of $\alpha = 0.47$ was used in this study. The respiration constant k is often described by an empirical relationship of the form:

$$k = k_0 \left(\frac{T_b}{10}\right)^a \left(\frac{O_b}{6}\right)^b \quad (13)$$

where k_0 is the multiplying factor (per day), T_b is the average temperature of the lower water column (10–20 m, $^{\circ}C$), O_b is the average oxygen concentration ($g\ O_2\ m^{-3} = mg\ O_2\ l^{-1}$) in the lower water column, and a and b are constants. The O_b value was computed by dividing the O_{tb} value (Eq. (2)) with the thickness of the lower water column (10 m). In this study, we have adopted the values of $k_0 = 0.008$, $a = 1.1$, and $b = 0.4$. The later two values were originally proposed for the Chesapeake Bay (Officer et al., 1985), while the k_0 value of 0.008 was the upper limit of the range of values for this constant proposed for Patuxent estuary (Boynton et al., 1980). Those estimates for k_0 , a and b provided a good fit to the benthic and epibenthic respiration rates observed in the coastal waters of the northern Gulf of Mexico (see Section 6.2).

3.2.5. Potential sedimentary carbon accumulation

Eq. (12) defines the net productivity as a surrogate for excess carbon in the upper water column (0–10 m) that is available for export to the lower water column (10–20 m). The instantaneous vertical carbon flux (S_f , $\text{g C m}^{-2} \text{ day}^{-1}$) due to the sedimentation of organic material from the upper water column may be described as:

$$S_f(t) = \alpha \text{NP}(t_0) \quad (14)$$

Accordingly, the balance equation for organic carbon in sediments (C_s , gC m^{-2}) may be written as:

$$\frac{\partial C_s}{\partial t} = S_f(t) - R(t) - E_c \quad (15)$$

where $R(t)$ is the respiration rate in the lower water column, expressed here in terms of carbon equivalents ($\text{gC m}^{-2} \text{ day}^{-1}$), and E_c ($\text{gC m}^{-2} \text{ day}^{-1}$) is the loss of sedimentary carbon due to resuspension and export. The continental shelf of the northern Gulf of Mexico is a highly dynamic system where wind-driven sediment resuspension may be a driving force in exporting sediments to the outer shelf and slope. Seasonal deposition rates can be locally high, but decadal sediment accumulation rates are significantly lower (Wiseman et al., 1999). In computing the organic carbon accumulation rates, we assumed that 50% of the sedimented organic carbon that is not subsequently decomposed is ultimately exported from the study area.

3.2.6. Model simulations

Eqs. (1), (2) and (15) represent a system of coupled, non-linear, ordinary differential equations. In simulation experiments, the equations were solved using the Runge–Kutta integration method of the fourth order, and an integration step of 0.01 month (0.3 days).

4. Data

Daily discharge data for the Mississippi River at Tarbert Landing for the period January 1955–May 2000, were obtained from the US Army Corps of Engineers. Tarbert Landing is located in

Mississippi, 13 km downstream from the inlet channel to the Old river control structure, where approximately one-third of the Mississippi River discharge is diverted to the Red river to form the Atchafalaya river. Wind speed data for the coastal station at Grand Isle, Louisiana, were obtained from the Louisiana Office of State Climatology. Grand Isle is within 65 km of our reference station C6. Monthly nitrate fluxes of the Mississippi River for January 1955–May 2000 were computed using N-NO_3 concentrations measured at St. Francisville, located ca. 430 km upstream from the Mississippi River Delta. Data sources and analytical methods used to determine nitrate concentrations are discussed in Turner and Rabalais (1991), Goolsby et al. (1999).

The data series used in model calibration were collected between June 1985 and November 1993 at a station C6 located in the core of the Gulf of Mexico hypoxic zone (Fig. 1). Those biweekly to monthly data series include ambient temperature and salinity as well as dissolved oxygen concentrations measured throughout the water column at depth intervals of 1–2 m. Standard water column profile data were obtained from a Hydrolab Surveyor or a SeaBird CTD system with SBE 13-01 (S/N 106) dissolved oxygen meter. The dissolved oxygen measurements were calibrated with Winkler titrations (Parsons et al., 1984) that were periodically carried out during hydrologic surveys.

5. Forcing functions

Model forcing functions included monthly values of the Mississippi River runoff (Q) and nitrate (N-NO_3) flux of the Mississippi River (Fig. 2), ambient surface and lower water column temperatures, and surface wind data (Table 1). The average monthly runoff of the Mississippi River increased significantly between 1955 and 2000. Generally, runoff was 29.6% lower during 1955–1972 (mean = $11\,822 \text{ m}^3 \text{ s}^{-1}$) when compared with 1973–2000 (mean = $15\,322 \text{ m}^3 \text{ s}^{-1}$).

The nitrate flux was computed from the runoff and the nitrate concentration values. It is evident from Fig. 2 that the N-NO_3 concentration in the

lower Mississippi River increased approximately three-fold between the 1960s and 1980s (Turner and Rabalais 1991; Goolsby et al., 1999), which is a change an order of magnitude greater than a change in runoff observed over the same period of time. The upward trend in N-NO₃ flux stabilized around 1985, and the concentrations remained relatively stable over the last 15–20 years. Nevertheless, there is a large interannual variability in N-NO₃ concentrations, which is most clearly evident when comparing the flood years, such as 1993, and the drought years, such as 1988 (Fig. 2). The average nitrate concentration during the flood of 1993, for example, was 1.72 mg N l⁻¹ (standard deviation(S.D.) = 0.46), which is significantly higher ($P < 0.001$) when compared with the drought of 1988 (mean = 0.92 mg N l⁻¹; S.D. = 0.57). The Mississippi River N-NO₃ flux closely

Table 2

Average monthly surface (T_s) and bottom(T_b) temperatures at station C6 (T_s = 0–1 m, and T_b = 10–20 m) and wind speed at station Grand Isle (W) for 1985–1993

Month	n	T_s (°C)	T_b (°C)	W (m s ⁻¹)
1	2	16.72	16.91	5.52
2	13	16.67	18.88	5.56
3	25	19.09	19.51	5.37
4	24	21.61	20.91	5.29
5	29	25.64	23.01	4.81
6	38	28.95	25.03	4.30
7	65	30.18	26.00	3.69
8	37	30.05	25.86	3.56
9	28	28.98	27.76	4.53
10	27	25.34	26.48	5.13
11	11	22.61	22.22	5.47
12	8	18.93	19.80	5.48

Number of observations is denoted by n , except for W , which is computed from hourly data.

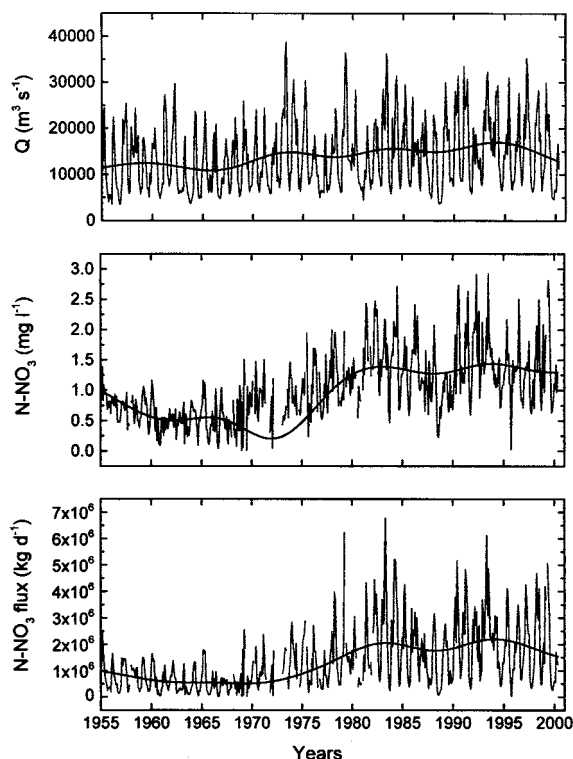


Fig. 2. Monthly averages of the Mississippi River runoff (Q), nitrate concentration (N-NO₃), and nitrate flux (N-NO₃ flux) for the period January 1955–May 2000. Smoothed curves were obtained by using a 48-point fast Fourier transform (FFT) filter.

follows the decadal and interannual changes in N-NO₃ concentrations (Fig. 2).

Water column temperatures and surface wind data were not available for the entire 1955–2000 period, and they were replicated from the observed 1985–1993 data (Table 2).

6. Model calibration and sensitivity analysis

The model was calibrated on the basis of a 1985–1993 data set for the Mississippi River and the Northern Gulf of Mexico. The 1985–1993 period included three average hydrologic years (1985, 1986 and 1989), a record flood year (1993, a 62-year record high discharge), 2 years with above average discharge (1990 and 1991), 3 years with below average discharge (1987, 1988 and 1992), and a record drought year (1988, a 52-year record low discharge). Given the time-span of the data, we considered the 1985–1993 data subset to be suitable for model calibration. A sensitivity analysis revealed that the model is highly sensitive to external forcing, yet sufficiently robust to withstand an order of magnitude change in the nitrate flux between successive months, such as those encountered during the flood of 1993.

6.1. Comparison of observed and predicted dissolved oxygen concentrations

Calibration results for surface and bottom oxygen concentrations are illustrated in Fig. 3. For the bottom layer (10–20 m), the model agrees exceptionally well with the observed values, both in terms of the annual and interannual variability. The agreement between the model and the data is also very good for the surface layer (0–10 m), with the exception of 1990, 1991 and 1993, for which the predicted summertime oxygen concentrations were somewhat higher than observed. As indicated previously, during 1990 and 1991 the Mississippi River discharge was above average, while 1993 was a record flood year.

6.2. Comparison of observed and predicted respiration rates in the lower water column

The model estimate for the average annual respiration rate of the lower water column (10–20 m) during 1985–1993 was $166 \text{ g O}_2 \text{ m}^{-2}$. A higher value of $262 \text{ g O}_2 \text{ m}^{-2} \text{ year}^{-1}$ was pre-

dicted by the model for the flood of 1993. These model estimates are in a good agreement with the respiration rates observed in the study area. Based on an analysis of oxygen budgets for the upper and the lower water column, Justić et al. (1997) estimated that the average annual respiration rate for the lower water column (10–20 m) is about $200 \text{ g O}_2 \text{ m}^{-2} \text{ year}^{-1}$. Turner and Rabalais (1998) and Turner et al. (1998) reported that the respiration rates in the lower water column varied between 0.0008 and $0.29 \text{ g O}_2 \text{ l h}^{-1}$. Dortch et al. (1994) reported an average oxygen uptake rate in the bottom water of $0.011 \text{ g O}_2 \text{ m}^{-3} \text{ day}^{-1}$. This converts to an annual value of $40 \text{ g O}_2 \text{ m}^{-2} \text{ year}^{-1}$, if the entire lower water column (10–20 m) is included. Rowe et al. (1992) reported an average sediment oxygen uptake rate of $17.7 \text{ ml O}_2 \text{ m}^{-2} \text{ h}^{-1}$ ($= 222 \text{ g O}_2 \text{ m}^{-2} \text{ year}^{-1}$) for the continental shelf of the northern Gulf of Mexico. We assume here that the above value also accounts for a large portion of anaerobic respiration, because most of the dissolved sulfide produced under anoxic conditions is re-oxidized by free dissolved oxygen (Berner, 1982). Thus, the upper estimate for the combined oxygen uptake of the lower water column (10–20 m), due to benthic and water column respiration, is on the order of $262 \text{ g O}_2 \text{ m}^{-2} \text{ year}^{-1}$. The latter value is essentially the same as the model estimate for 1993.

7. Model simulations

7.1. Simulated decadal changes in surface and bottom oxygen concentrations

Model simulations for a station within the core of the present day hypoxic zone (C6, Fig. 1) indicated a decadal trend of increase in the oxygen concentrations in the upper water column (0–10 m) and decrease in the lower water column (10–20 m) (Fig. 4). The annual average oxygen concentration at 10–20 m depth decreased from 6.6 mg l^{-1} in 1955–1965, 6.2 mg l^{-1} in 1965–1975, 4.9 mg l^{-1} in 1975–1985, to 4.2 mg l^{-1} during 1990–2000. As expected, the differences in summertime oxygen concentrations between those periods are even greater. The average oxygen

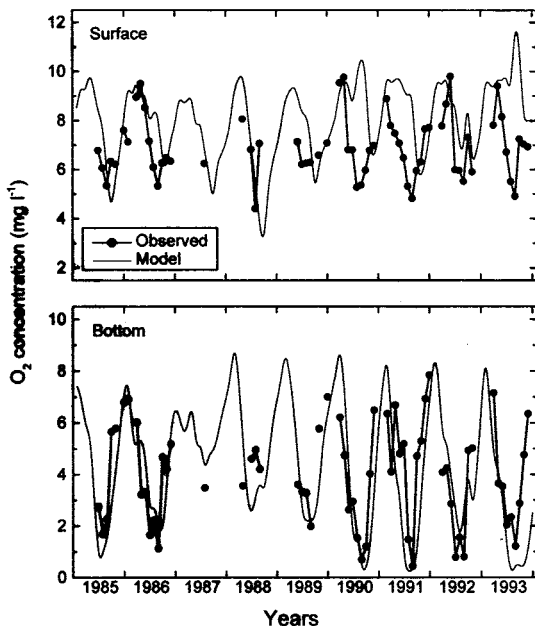


Fig. 3. Observed and predicted monthly averages of surface (0–10 m) and bottom (10–20 m) oxygen concentrations at station C6 for the period June 1985–November 1993.

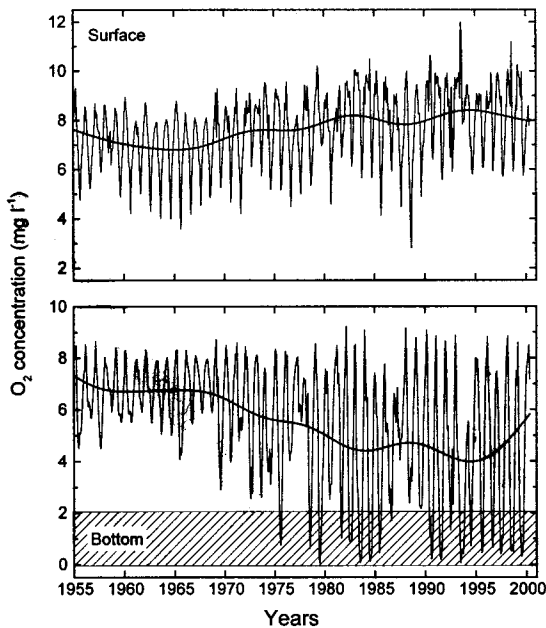


Fig. 4. Simulated changes in the average surface (0–10 m) and bottom (10–20 m) oxygen concentration at station C6 for the period January 1955–May 2000. Shaded area in the lower chart denotes hypoxic conditions ($< 2 \text{ mg O}_2 \text{ l}^{-1}$) in bottom waters. Smoothed curves were obtained by using a 48-point FFT filter.

concentration in the lower water column during August decreased from 5.8 mg l^{-1} in 1955–1965, 4.2 mg l^{-1} in 1965–1975, 1.9 mg l^{-1} in 1975–1985, to 0.9 mg l^{-1} during 1990–2000. The model has identified the mid 1970s as a start of the recurring hypoxia ($< 2 \text{ mg O}_2 \text{ l}^{-1}$) in the lower water column. This result should, however, be interpreted with caution, because the model only predicts the average oxygen concentration for the entire lower water column. It is probable that hypoxia in the near bottom waters was sporadically present during the late 1960s and early 1970s, and perhaps even earlier than that (Fig. 4).

The model results also suggest that the annual average oxygen concentration of the upper water column (0–10 m) increased from 7.0 mg l^{-1} in 1955–1965, 7.3 mg l^{-1} in 1965–1975, 7.9 mg l^{-1} in 1975–1985, to 8.4 mg l^{-1} during 1990–2000.

7.2. Simulated decadal changes in sedimentary carbon accumulation

The model simulations indicated a decadal trend of increase in the sedimentary organic carbon accumulation rates (Fig. 5). The average organic carbon accumulation rate increased from $0.7 \text{ gC m}^{-2} \text{ year}^{-1}$ in 1955–1965, $1.8 \text{ gC m}^{-2} \text{ year}^{-1}$ in 1965–1975, $7.4 \text{ gC m}^{-2} \text{ year}^{-1}$ in 1975–1985 to $9.8 \text{ gC m}^{-2} \text{ year}^{-1}$ during 1990–2000. There seems to be a good agreement between the model and the observed data, especially for the period prior to 1985 (Fig. 5). Also, there is a high coherence between changes in sedimentary

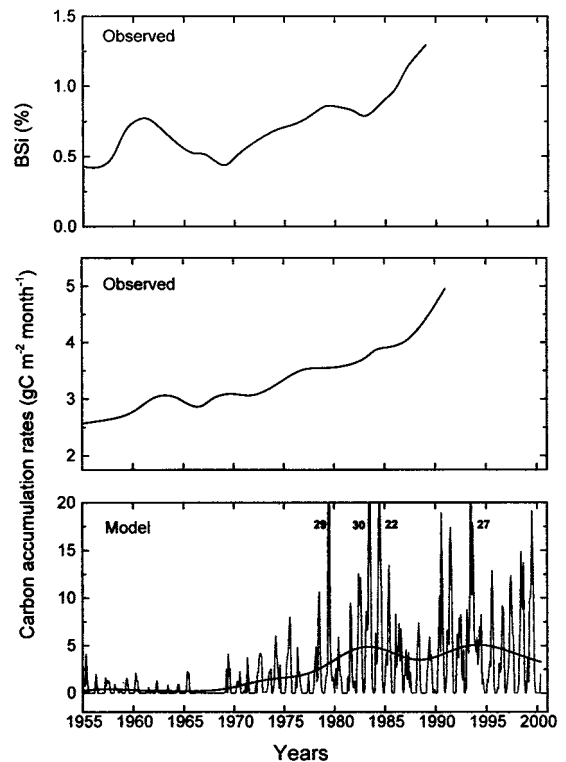


Fig. 5. Upper and center figure charts—observed decadal changes in the biogenic silica (BSi) concentration (upper, from Turner and Rabalais, 1994) and sedimentary organic carbon accumulation rates (center, from Eadie et al., 1994) at two stations within the area of chronic hypoxia. Lower chart shows potential carbon accumulation rates predicted by the model. Smoothed curve was obtained by using a 48-point FFT filter. Numbers at the top of the chart indicate values outside the chosen y-axis interval.

carbon accumulation rates and changes in bottom oxygen concentrations (Figs. 4 and 5).

8. Discussion

The results of model simulations indicated that the annual average oxygen concentration at 10–20 m depth decreased from 6.6 mg l^{-1} in 1955–1965 to 4.2 mg l^{-1} during 1990–2000 (Fig. 4), and the model identified the mid 1970s as a start of the recurring hypoxia ($< 2 \text{ mg O}_2 \text{ l}^{-1}$) in the lower water column (10–20 m). Comprehensive long-term data series to fully examine past changes in the bottom oxygen concentrations, such as those for the northern Adriatic Sea (Justić et al., 1987), are not available for the northern Gulf of Mexico. Nevertheless, the timing of first reports documenting hypoxia in localized areas of the shelf seems to be in good agreement with model predictions. Hypoxia in the coastal bottom waters of the northern Gulf of Mexico was first observed in the early 1970s, during routine environmental monitoring stimulated by oil production and transportation studies. In the mid 1970s, Turner and Allen (1982) documented summertime hypoxia over larger areas of the shelf. Between 1985 and 1992 the areal extent of the hypoxic zone averaged between 7000 and 9000 km^2 , and has increased since to a record size of 20 000 km^2 in 1999 (Rabalais et al., 1999).

These model results suggest that hypoxia in river dominated coastal waters develops in response to nutrient-enhanced surface primary productivity, which is also manifested in a high vertical carbon flux. This paradigm is additionally supported by other modeling studies (e.g. Bierman et al., 1994) and by the retrospective analyses of sedimentary records. The analyses of ^{210}Pb -dated sediment cores collected in the vicinity of the Mississippi River Delta demonstrated a substantial increase in the organic carbon accumulation rates, from about $30 \text{ gC m}^{-2} \text{ year}^{-1}$ in the 1950s to $50\text{--}70 \text{ gC m}^{-2} \text{ year}^{-1}$ at present (Fig. 5; Eadie et al., 1994). Interestingly, the rate of carbon accumulation is significantly higher at a station within the area of chronic hypoxia ($\sim 70 \text{ gC m}^{-2} \text{ year}^{-1}$), in comparison with an adjacent site

at which hypoxia has not been documented ($\sim 50 \text{ gC m}^{-2} \text{ year}^{-1}$). The $\delta^{13}\text{C}$ partitioning of organic carbon into terrestrial and marine fractions further indicated that the increase in accumulation for both cores is exclusively in the marine fraction.

Parallel evidence of historical changes in the river-dominated coastal waters of the northern Gulf of Mexico has been obtained from the skeletal remains of diatoms sequestered as biologically bound silica (BSi). BSi accumulation rates in sediments adjacent to the Mississippi Delta have doubled since the 1950s, indicating greater diatom flux from the euphotic zone (Fig. 5; Turner and Rabalais, 1994). Lastly, stratigraphic records of benthic foraminifera, i.e. the relative dominance of two common species of *Ammonia* and *Elphidium* (A–E index), indicate an overall increase in the bottom oxygen stress in the same region (Sen Gupta et al., 1996).

The above changes in the accumulation rates of organic carbon and BSi in the sediments, along with biostratigraphic records, present strong evidence for the hypothesis that the productivity of the surface waters in the vicinity of the Mississippi River Delta has increased since 1950s. Importantly, the above changes have occurred coincidentally with changes in riverine nutrient fluxes (Fig. 2). The oxygen deficiency in the bottom waters has increased in response to a higher vertical carbon flux (Fig. 5), thus demonstrating the progression of benthic–pelagic coupling as a result of decadal anthropogenic impact.

9. Conclusions

We have developed a simple eutrophication model that accurately describes changes in surface and bottom oxygen concentrations for a station within the core of the Gulf of Mexico hypoxic zone. A sensitivity analysis revealed that the model is highly sensitive to external forcing, yet sufficiently robust to withstand order of magnitude changes in the nitrate flux of the Mississippi River. Model simulations indicated that bottom water hypoxia in the northern Gulf of Mexico has intensified in recent historical time, as a probable

consequence of increased net productivity and increase in the vertical flux of the organic carbon. Apparently, the long-term increase in riverine nutrient fluxes has been the primary factor controlling this historical decline in oxygen concentrations. This modeling study supports the hypothesis that riverine nutrient fluxes, via their influence on net productivity of the upper water column, play a major role in controlling the development of bottom water hypoxia and accumulation of organic carbon in coastal sediments.

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